Customized FORM PTO-1390 U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE

TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US) CONCERNING A FILING UNDER 35 U.S.C. 371

ATTORNEY DOCKET NO.	U.S. APPLICATION NO. (If known, see 37 CFR 1.5)
P07222US00/LRP	09/856361

INTERNATIONAL APPLICATION NO.	INTERNATIONAL FILING DATE	PRIORITY DATE CLAIMED
PCT/JP99/06503	22 November 1999	24 November 1998

TITLE OF INVENTION: ETCHING SOLUTION, ETCHED ARTICLE AND METHOD FOR ETCHED ARTICLE

APPLICANT(S) FOR DO/EO/US: KEZUKA ET AL.

Applicant herewith submits to the US Designated/Elected Office (DO/EO/US) the following items and other information:

X 1. This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.

2. This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 USC 371.

X 3. This express request to begin national examination procedures (35 USC 371(f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 USC 371(b) and PCT Art. 22 and 39(1).

X 4. A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date.

5. A **copy** of the International Application as filed (35 U.S.C. 371 (c)(2))
   a. is transmitted herewith (required only if not transmitted by the International Bureau).
   X b. has been transmitted by the International Bureau.
   c. is not required, as the application was filed in the United States Receiving Office (RO/US).

X 6. A **translation** of the International Application into English (35 U.S.C. 371(c)(2)).

7. Amendments to the claims of the International Appln. under PCT Article 19 (35 USC 371 (c)(3))
   a. are transmitted herewith (required only if not transmitted by the International Bureau).
   b. have been transmitted by the International Bureau.
   c. have not been made; however, the time limit for making such amendments had NOT expired.
   d. have not been made and will not be made.

8. A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).

X 9. An **oath** or declaration of the inventor(s) (35 U.S.C. 371(c)(4)).

10. A translation of the annexes to the Int'l Prelim. Exam. Report under PCT Article 36 (35 U.S.C. 371(c)(5)).

Items 11 to 20 below concern document(s) or information included:

11. An **Information Disclosure Statement** under 37 C.F.R. 1.97 and 1.98.

X 12. An **Assignment** document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.

X 13. A **First preliminary amendment**.

14. A Second or Subsequent preliminary amendment.

15. A substitute specification.

X 16. A change of power of attorney and/or address letter.

17. A computer-readable form of the sequence listing in accordance with PCT Rule 13ter.2 & 35 USC 1.821-825.

18. A second copy of the published international application under 35 USC 154(d)(4).

19. A second copy of the English translation of the international application under 35 USC 154(d)(4).

20. Other items or information:

A copy of the Notification of Missing Requirements under 35 U.S.C. 371.

X In the event that a petition for extension of time is required to be submitted herewith, and in the event that a separate petition does not accompany this response, applicant hereby petitions under 37 CFR 1.136(a) for an extension of time of as many months as are required to render this submission timely. Any fee is authorized in 17(c).

Date: May 22, 2001

LARSON & TAYLOR, PLC • 1199 North Fairfax St. • Suite 900 • Alexandria, VA 22314

U.S. APPLICATION NO. (if known)	INTERNATIONAL APPLICATION NO.	ATTORNEY DOCKET NO.
09/856361	PCT/JP99/06503	P07222US00/LRP

		CALCULATIONS *PTO USE ONLY*
X	21. **The following fees are submitted:**	
X	**Basic National Fee** (37 CFR 1.492 (a) (1)-(5):	
	Neither Int'l Prelim. Exam. fee nor Int'l Search fee paid to USPTO $1000	
X	Search Report has been prepared by the EPO or JPO $ 860	
	No Int'l Prelim. Ex. fee paid to USPTO but Int'l Search fee paid to USPTO $ 710	
	International preliminary examination fee paid to USPTO $ 690	
	Int'l Prelim. Ex. fee paid to USPTO & all claims satisfied PCT Art. 33(1)-(4) $ 100	
	ENTER APPROPRIATE BASIC FEE AMOUNT =	$ 860
	Surcharge of $130 for furnishing the oath or declaration later than [ ] 20 mos. from the earliest claimed priority date (37 CFR 1.492(e)). [ ] 30 mos. +	$ 0

CLAIMS	*NUMBER FILED*	*NUMBER EXTRA*	*RATE*	
Total Claims	15 - 20 =	0	X **$18** =	$ 0
Independent Claims	1 - 03 =	0	X **$80** =	$ 0
Multiple Dependent Claim(s) (if applicable)			+ **$270** =	$ 0
			TOTAL OF ABOVE CALCULATIONS =	**$ 860**
Applicant claims small entity status. See 37 CFR 1.27. The fees indicated above are reduced by ½.			-	$
			SUBTOTAL =	**$ 860**
Processing fee of **$130** for furnishing the **English translation** later than [ ] 20 mos. from the earliest claimed priority date (37 CFR 1.492(f)). [ ] 30 mos. +				$ 0
			TOTAL NATIONAL FEE =	**$ 860**
X Fee for recording the enclosed **assignment** (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). **$40** per property			+	$ 40
			TOTAL FEES ENCLOSED =	**$ 900**
			Amount to be *Refunded*	$
			Charged	$

X a. A **check** in the amount of $900.00 to cover the above fees is enclosed.

b. Please charge my Deposit Account No. 12-0555 in the amount of $ to cover the above fees.

X c. The Commissioner is hereby authorized to charge any additional fees required or credit overpayment to Deposit Account No. 12-0555.

Note: *Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.*

SEND ALL CORRESPONDENCE TO:

Linda R. Poteate

At the address (below) of **CUSTOMER NO. 000881.**

LARSON & TAYLOR, PLC
1199 NORTH FAIRFAX ST.
SUITE 900
ALEXANDRIA, VA 22314

SIGNATURE: Douglas E. Jackson

NAME: Douglas E. Jackson

REG. NO.: 28,518

PHONE NO.: 703-739-4900

Date: May 22, 2001

Customized FORM PTO-1390

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Patent

In re patent application of: KEZUKA ET AL.

Serial No.: Unassigned — Examiner: Unassigned

Filed: May 22, 2001 — Art Unit: Unassigned

For: ETCHING SOLUTION, ETCHED ARTICLE AND METHOD FOR ETCHED ARTICLE — Docket No.: P07222US00/LRP

PRELIMINARY AMENDMENT

Assistant Commissioner of Patents

Washington, D.C. 20231

SIR:

Prior to examination, please amend the above-identified application as follows:

IN THE CLAIMS

A clean version of all amended claim 14 is provided herewith in **Attachment A**. It will be noted that claim 14 has been amended relative to the previously provided version submitted with the application shown by the marked up version thereof in **Attachment B** provided herewith.

REMARKS

The present Amendment is made to eliminate multiple dependency in the claims.

Respectfully submitted,

Date: May 22, 2001

By: Douglas E. Jackson Jr.
Registration No.: 28,518

LARSON & TAYLOR, PLC • 1199 North Fairfax St. • Suite 900 • Alexandria, VA 22314 • (703) 739-4900

ATTACHMENT A

Clean Replacement/New Claims

Following herewith is a marked up copy of each rewritten claim.

14. (AMENDED) A method for producing an etched article by etching an article with the etching solution as defined in claim 1.

ATTACHMENT B

Marked Up Replacement Claims

Following herewith is a marked up copy of each rewritten claim.

14. (AMENDED) A method for producing an etched article by etching an article with the etching solution as defined in ~~any of claims 1-13~~ claim 1.

DESCRIPTION

Etching solution, etched article and method for etched article

TECHNICAL FIELD

The present invention relates to an etching solution, a method for producing an etched article and an etched article produced by the method, more specifically, an etching solution and a method for producing an etched article for etching doped oxide films such as a boron phosphosilicate glass (BPSG) film and undoped oxide films such as a thermal oxide (THOX) film at the same etch rate or similar etch rate, and an etched article produced by the method.

BACKGROUND ART

Conventionally, as etchants for silicon wafers and the like have been used buffered hydrofluoric acids comprising HF (50-wt.% aqueous solution) and NH_4F (40-wt.% aqueous solution) at such a ratio that can achieve a desired etch rate.

However, the buffered hydrofluoric acids etch doped oxide films such as BSG (boron silicate glass film), BPSG, PSG (phosphosilicate glass film), AsSg (phosphosilicate glass film) and the like faster than they etch undoped oxide films such as TEOS (oxide film formed by CVD method using tetraethoxysilane gas) and

like USG, THOX and like. Therefore, the buffered hydrofluoric acids can not etch the doped oxide films and undoped oxide films at the same rate.

An object of the present invention is to provide an etching solution and an etching method for etching undoped oxide films such as TEOS, THOX and the like and oxide films doped with impurities at the same rate.

DISCLOSURE OF INVENTION

The present invention relates to the items 1-15 listed below.

Item 1. An etching solution having a thermal oxide (THOX) film etch rate and boron phosphosilicate glass (BPSG) film etch rate at 25°C of 100Å/min or lower and a ratio of (BPSG etch rate) / (THOX etch rate) of 1.5 or lower.

Item 2. The etching solution according to item 1 comprising at least one member selected from the group consisting of a fluoride salt and a bifluoride salt.

Item 3. The etching solution according to item 1, wherein a solvent of the etching solution has a relative dielectric constant of 35 or lower.

Item 4. The etching solution according to item 1 comprising at least one member selected from the group consisting of an organic acid and an organic solvent

having a hetero atom.

Item 5. The etching solution according to item 1 comprising (i) ammonium hydrogenfluoride, (ii) water and (iii) at least one member selected from the group consisting of an organic acid and an organic solvent having a hetero atom, the water being contained in a concentration of 3% by weight or lower.

Item 6. The etching solution according to item 1 comprising ammonium hydrogenfluoride, water and isopropyl alcohol, the water being contained in a concentration of 3% by weight or lower.

Item 7. The etching solution according to item 1 comprising ammonium hydrogenfluoride, water and ethanol, the water being contained in a concentration of 3% by weight or lower.

Item 8. The etching solution according to item 1 comprising ammonium hydrogenfluoride, water and acetone, the water being contained in a concentration of 3% by weight or lower.

Item 9. The etching solution according to item 1 comprising (i) ammonium fluoride and (ii) at least one member selected from the group consisting of an organic acid and an organic solvent having a hetero atom.

Item 10. The etching solution according to item 1 comprising (i) ammonium fluoride, (ii) water and (iii) at

least one member selected from the group consisting of an organic acid and an organic solvent having a hetero atom, the water being contained in a concentration of 10% by weight or lower.

Item 11. The etching solution according to item 1 comprising ammonium fluoride, water and ethanol, the water being contained in a concentration of 10% by weight or lower.

Item 12. The etching solution according to item 1 comprising ammonium fluoride, water and isopropyl alcohol, the water being contained in a concentration of 10% by weight or lower.

Item 13. The etching solution according to item 1 comprising ammonium fluoride, water and acetic acid, the water being contained in a concentration of 1.5% by weight or lower.

Item 14. A method for producing an etched article by etching an article with the etching solution as defined in any of items 1-13.

Item 15. An etched article which is produced by the method of item 14.

The etching solution of the present invention has the ratio of BPSG etch rate / THOX etch rate at 25°C of 1.5 or lower, preferably 1.3 or lower, more preferably 1.2 or lower, still more preferably 1.1 or lower,

particularly 1.05 or lower.

The BPSG is used for measuring etch rate after being formed as a film and annealed.

The etching solution of the present invention satisfies the above ratio of the etch rates, and also has a THOX etch rate and a BPSG etch rate at 25°C of 100Å/min or lower, preferably 80Å/min or lower, still more preferably 60Å/min or lower, particularly 50Å/min or lower. The lower limit of the etch rates at 25°C is 0.01Å/min or higher, preferably 0.1Å/min or higher, still more preferably 1Å/min or higher.

The etch rate of the etching solution of the invention can be determined by etching BPSG and THOX with the etching solution at 25°C and dividing the difference in the film thickness before and after being etched by the etch time.

Examples the fluoride salt and bifluoride salt of the present invention include metal salts, ammonium salts and quaternary ammonium salts. Preferable examples of the metal salts include those which have high solubility, such as potassium fluorides, sodium fluoride, potassium hydrogenfluoride, sodium hydrogenfluoride and the like. Examples of the ammonium salts include ammonium fluoride and ammonium hydrogenfluoride (ammonium hydrogenfluoride). Examples of the quaternary ammonium

salts include tetramethylammonium fluoride, methylamine hydrofluoride, 2-hydroxyethyltrimethylammonium fluoride, tetramethylammonium hydrogenfluoride and the like.

In the present invention, the relative dielectric constant is that of the solvent (an organic solvent having a hetero atom, an organic acid or water) itself at 25°C.

The relative dielectric constant is 35 or lower, preferably 25 or lower, more preferably 21 or lower.

Ammonium hydrogenfluoride to be added to the etching solution of the invention may be in the form of crystals or an aqueous solution. Alternatively, a stoichiometric amount of ammonium fluoride and HF may be added to the etching solution to form ammonium hydrogenfluoride within the solution.

The ammonium fluoride to be added to the etching solution of the invention may be in the form of crystals or an aqueous solution.

Examples of the organic acid include acetic acid (relative dielectric constant: 6.15 (20°C)), propionic acid (relative dielectric constant: 3.4 (40°C)), butyric acid (relative dielectric constant: 2.97(20°C)), isobutyric acid (relative dielectric constant: 2.73(40°C)), valeric acid, caproic acid (relative dielectric constant: 2.63(71°C)), caprylic acid (relative

dielectric constant: 2.45(20°C)), monochloroacetic acid (relative dielectric constant: 21 (20°C)), dichloroacetic acid (relative dielectric constant: 8.08(20°C)), trichloroacetic acid (relative dielectric constant: 4.6 (60°C)), monofluoroacetic acid, difluoroacetic acid, trifluoroacetic acid, α-chlorobutyric acid, β-chlorobutyric acid, γ-chlorobutyric acid, lactic acid (relative dielectric constant: 22(70°C)), glycolic acid, pyruvic acid, glyoxalic acid, acrylic acid and like monocarboxylic acids, methanesulfonic acid, toluenesulfonic acid and like sulfonic acids, oxalic acid, succinic acid, adipic acid, tartaric acid, citric acid and like polycarboxylic acids.

Examples of the organic solvent having a hetero atom include methanol (relative dielectric constant: 32.6 (25°C)), ethanol (relative dielectric constant: 24.6 (25°C)), isopropyl alcohol (IPA, relative dielectric constant: 19.9 (25°C)), 1-propanol (relative dielectric constant: 22.2 (25°C)), 1-butanol (relative dielectric constant: 17.1 (25°C)), 2-butanol (relative dielectric constant: 15.5 (19°C)), t-butanol (relative dielectric constant: 11.4 (19°C)), 2-methyl-1-propanol (relative dielectric constant: 17.95 (20°C)), 1-pentanol (relative dielectric constant: 13.9 (25°C)), 1-hexanol (relative dielectric constant: 13.3 (25°C)), 1-heptanol, 4-heptanol,

1-octanol (relative dielectric constant: 10.34 (20°C)), 1-nonylalcohol, 1-decanol, 1-dodecanol and like alcohols; ethylene glycol (relative dielectric constant: 37.7 (25°C)), 1,2-propanediol (relative dielectric constant: 32.0 (20°C)), 2,3-butanediol, glycerin (relative dielectric constant: 42.5 (25°C)) and like polyols, acetone (relative dielectric constant: 20.7 (25°C)), acetylacetone, methyl ethyl ketone (relative dielectric constant: 18.51 (20°C)) and like ketones; acetonitrile (relative dielectric constant: 37.5 (20°C)), propionitrile (relative dielectric constant: 29.7 (20°C)), butyronitrile (relative dielectric constant: 20.3 (20°C)), isobutyronitrile (relative dielectric constant: 20.4 (20°C)), benzonitrile (relative dielectric constant: 25.2 (25°C)) and like nitriles; formaldehyde, acetaldehyde, propionaldehyde and like aldehydes; ethylene glycol monomethyl ether, ethylene glycol monoethyl ether and like alkylene glycol monoalkyl ethers; tetrahydrofuran (relative dielectric constant: 7.6 (25°C)), dioxane (relative dielectric constant: 2.2 (25°C)) and like ethers, trifluoroethanol, pentafluoropropanol, 2,2,3,3-tetrafluoropropanol and like fluorine alcohols, sulfolane (relative dielectric constant: 43.3 (30°C)), nitromethane (relative dielectric constant: 35.87 (30°C)) and the like.

The relative dielectric constant of water is

78.3 (25°C).

The content of ammonium hydrogenfluoride is about 0.01-5% by weight, preferably about 0.01-2.5% by weight.

The content of ammonium fluoride is preferably about 0.01-4% by weight, more preferably about 0.01-2% by weight.

The water content is preferably 10% by weight or lower, more preferably about 3% by weight or lower.

The content of the organic acid is preferably 85% by weight or higher, more preferably 95% by weight or higher.

The content of the organic solvent having a hetero atom is preferably 85-99.9% by weight, more preferably 95-99.99% by weight.

The total content of the organic acid and the organic solvent having a hetero atom is preferably 85-99.9% by weight, more preferably 95-99.99% by weight.

Preferable etching solutions of the present invention and their compositions are shown below.

- Ammonium hydrogenfluoride : IPA : water = 0.01-5% by weight : 92-99.99% by weight : 0-3% by weight;
- Ammonium hydrogenfluoride : ethanol : water = 0.01-5% by weight : 92-99.99% by weight : 0-3% by weight;
- Ammonium hydrogenfluoride : acetone : water = 0.01-5%

by weight : 92-99.99% by weight : 0-3% by weight;

- Ammonium fluoride : IPA : water = 0.01-4% by weight : 86-99.99% by weight : 0-10% by weight;
- Ammonium fluoride : acetic acid : water = 0.01-4% by weight : 94.5-99.99% by weight : 0-1.5% by weight;
- Ammonium fluoride : ethanol : water = 0.01-5% by weight : 86-99.99% by weight : 0-10% by weight.

The etching solution of the invention can be suitably used for etching oxide films of an article to be etched comprising an oxide film (BSG, BPSG, PSG, AsSG, etc.) doped with B, P, As and the like and an undoped oxide film such as USG such as THOX, TEOS and like.

In the etching method of the present invention, the temperature of the etching solution is about 15-40°C, and the etch time is about 0.25-10 minutes.

Examples of the article to be etched include single crystalline silicon wafers, gallium-arsenic wafers and like wafers, especially articles comprising a doped oxide film (BSG, BPSG, PSG, AsSG, etc.) and an undoped oxide film (THOX, TEOS and like USG).

The present invention can provide an etching solution and a method for producing an etched article for etching THOX, TEOS and like USG and a oxide film doped with impurities, such as BPSG, BSG and the like at nearly the same rate, and an etched article produced by the

method.

BEST MODE FOR CARRYING OUT THE INVENTION

The present invention will be explained in more detail referring to Examples and Comparative Examples below.

Hereinafter, the relative dielectric constant is that of the solvent (an organic solvent having a hetero atom, an organic acid or water) itself at 25°C.

The etch rate was determined by measuring the thickness of the films before and after the etching using an Auto EL-III ellipsometer manufactured by Rudolf Research.

Examples 1-3 and Comparative Examples 1-2

Ammonium hydrogenfluoride ($NH_4F \cdot HF$), water and an organic solvent having a hetero atom were mixed at the ratios shown in Table 1. The mixtures were filtrated using a filter paper to remove crystals therefrom, giving etching solutions. The etch rate and etch selectivity of the etching solutions were determined using two test substrates: one comprising a silicon substrate and a THOX film formed thereon, the other comprising a silicon substrate and a BPSG film formed thereon.

The results are shown in Table 1.

Table 1

Ammonium hydrogenfluoride/organic solvent/water etching solution

	Organic solvent	Relative dielectric constant	$NH_4F \cdot HF$ concentration (%)	Organic solvent concentration (%)	Water concentration (%)	THOX etch rate (Å/min.)	BPSG etch rate (Å/min.)	Selectivity
Ex. 1	IPA	19.9	2.28	96.22	1.5	58	52	0.90
Ex. 2	Acetone	20.7	2.28	96.22	1.5	16	18	1.13
Ex. 3	Ethanol	24.6	2.28	96.22	1.5	31	37	1.19
Comp. Ex. 1	Ethanol	32.7	2.28	96.22	1.5	63	120	1.90
Comp. Ex. 2	(Water)	78.3	2.28	0	97.72	44	358	8.14

Examples 4-7 and Comparative Example 3

Ammonium fluoride (NH_4F), water and an organic solvent having a hetero atom were mixed at the ratios shown in Table 2. The mixtures were filtrated using a filter paper to remove crystals therefrom, giving etching solutions. The etch rate and selectivity of the etching solutions were determined using two test substrates: one comprising a silicon substrate and a THOX film formed thereon, the other comprising a silicon substrate and a BPSG film formed thereon. The results are shown in Table 2.

Table 2

Ammonium fluoride/organic solvent/water etching solution

	Organic solvent	Relative dielectric constant	NH_4F concentration (%)	Organic solvent concentration (%)	Water concentration (%)	THOX etch rate (Å/min.)	BPSG etch rate (Å/min.)	Selectivity
Ex. 4	Acetic acid	6.2	1.85	98.15	0	77	70	0.91
Ex. 5	IPA	19.9	1.48	93.52	5.0	8	10	1.25
Ex. 6	Ethanol	24.6	1.48	93.52	5.0	11	15	1.36
Ex. 7	Ethanol	32.7	1.47	97.02	1.5	8	11	1.38
Comp. Ex. 3	(Water)	78.3	1.48	0	98.52	<3	<3	--

Example 8 and Comparative Examples 4-7

Ammonium hydrogenfluoride ($NH_4F \cdot HF$), ammonium fluoride (NH_4F), water and an organic solvent having a hetero atom were mixed at the ratios shown in Table 3. The mixtures were filtrated using a filter paper to remove crystals therefrom, giving etching solutions. The etch rate and selectivity of the etching solutions were determined using two test substrates: one comprising a silicon substrate and a THOX film formed thereon, the other comprising a silicon substrate and a BPSG film formed thereon. The results are shown in Table 3.

Table 3

Ammonium hydrogenfluoride/ammonium fluoride/organic solvent/water etching solution

	Organic solvent	Relative dielectric constant	$NH_4F \cdot HF$ concentration (%)	NH_4F concentration (%)	Organic solvent concentration (%)	Water concentration (%)	THOX etch rate (Å/min.)	BPSG etch rate (Å/min.)	Selectivity
Ex. 8	Ethanol	24.6	0.7125	1.48	92.81	5.0	28	35	1.25
Comp. Ex. 4	(Water)	78.3	0.7125	9.5375	0	89.75	59	163	2.76
Comp. Ex. 5	(Water)	78.3	0.7125	19.5375	0	79.75	63	153	2.43
Comp. Ex. 6	(Water)	78.3	0.7125	29.5375	0	69.75	59	107	1.81
Comp. Ex. 7	(Water)	78.3	0.7125	39.5375	0	59.75	43	66	1.53

Examples 9-13 and Comparative Example 8

Ammonium hydrogenfluoride ($NH_4F \cdot HF$), water and IPA were mixed at the ratios shown in Table 4. The mixtures were filtrated using a filter paper to remove crystals therefrom, giving etching solutions. The etch rate and selectivity of the etching solutions were determined using two test substrates: one comprising a silicon substrate and a THOX film formed thereon, the other comprising a silicon substrate and a BPSG film formed thereon. The results are shown in Table 4.

Table 4

Ammonium hydrogenfluoride/2-propanol/organic solvent/water etching solution

	Organic solvent	Relative dielectric constant	$NH_4F \cdot HF$ concentration (%)	Organic solvent concentration (%)	Water concentration (%)	THOX etch rate (Å/min.)	BPSG etch rate (Å/min.)	Selectivity
Ex. 9	IPA	19.9	0.1425	98.8575	1.0	19	18	0.95
Ex. 10	IPA	19.9	0.1425	98.3575	1.5	12	13	1.08
Ex. 11	IPA	19.9	0.1425	97.8575	2.0	17	23	1.35
Ex. 12	IPA	19.9	0.1425	97.3575	2.5	24	33	1.38
Ex. 13	IPA	19.9	0.1425	96.8575	3.0	24	36	1.50
Comp. Ex. 8	IPA	19.9	0.1425	94.3575	5.0	23	43	1.87

Examples 14-15 and Comparative Examples 9-10

Ammonium fluoride (NH_4F), water and ethanol were mixed at the ratios shown in Table 5. The mixtures were filtrated using a filter paper to remove crystals therefrom, giving etching solutions. The etch rate and selectivity of the etching solutions were determined using two test substrates: one comprising a silicon substrate and a THOX film formed thereon, the other comprising a silicon substrate and a BPSG film formed thereon. The results are shown in Table 5.

Table 5

Ammonium fluoride/ethanol/water etching solution

	Organic solvent	Relative dielectric constant	NH_4F concentration (%)	Organic solvent concentration (%)	Water concentration (%)	THOX etch rate (Å/min.)	BPSG etch rate (Å/min.)	Selectivity
Ex. 14	Ethanol	24.6	1.48	97.02	1.5	8	10	1.25
Ex. 15	Ethanol	24.6	1.48	88.52	10.0	13	18	1.38
Comp. Ex. 9	Ethanol	24.6	1.48	83.52	15.0	12	29	2.42
Comp. Ex. 10	Ethanol	24.6	1.48	68.52	30.0	<3	27	--

Examples 16-19 and Comparative Examples 11-12

Ammonium fluoride (NH_4F), water and acetic acid were mixed at the ratios shown in Table 6. The mixtures were filtrated using a filter paper to remove crystals therefrom, giving etching solutions. The etch rate and selectivity of the etching solutions were determined using two test substrates: one comprising a silicon substrate and a THOX film formed thereon, the other comprising a silicon substrate and a BPSG film formed thereon. The results are shown in Table 6.

Table 6

Ammonium fluoride/acetic acid/water etching solution

	Organic solvent	Relative dielectric constant	NH_4F concentration (%)	Organic solvent concentration (%)	Water concentration (%)	THOX etch rate (Å/min.)	BPSG etch rate (Å/min.)	Selectivity
Ex. 16	Acetic acid	6.2	0.2775	99.7225	0	27	38	1.41
Ex. 17	Acetic acid	6.2	0.37	99.63	0	72	67	0.93
Ex. 18	Acetic acid	6.2	0.37	96.3	1.0	73	95	1.31
Ex. 19	Acetic acid	6.2	0.925	99.075	0	73	69	0.95
Comp. Ex. 11	Acetic acid	6.2	3.7	96.3	0	104	101	0.97
Comp. Ex. 12	Acetic acid	6.2	0.37	96.3	3.0	75	154	2.05

Example 20 and Comparative Examples 13-14

Ammonium hydrogenfluoride ($NH_4F \cdot HF$), water and an organic solvent having a hetero atom were mixed at the ratios shown in Table 7. The mixtures were filtrated using a filter paper to remove crystals therefrom, giving etching solutions. The etch rate and selectivity of the etching solutions were determined using test substrates each comprising a silicon substrate and one of undoped oxide films (THOX, TEOS) and doped oxide films (BSG, BPSG, PSG, AsSG) formed thereon. The results are shown in Table 7.

Table 7

Etch rates of doped films and undoped films

	Ex. 20	Comp. Ex. 13	Comp. Ex. 14
Organic solvent	IPA	(Water)	(Water)
Relative dielectric constant	19.9	78.3	78.3
$NH_4F \cdot HF$ concentration (%)	0.57	0.57	0.7125
NH_4F concentration (%)	0	0	39.5375
Organic solvent concentration (%)	98.675	0	0
Water concentration (%)	0.755	99.43	59.75
Etch rate			
THOX etch rate (Å/min.)	38	22	43
TEOS etch rate (Å/min.)	47	39	61
BSG etch rate (Å/min.)	48	171	93
BPSG etch rate (Å/min.)	39	179	66
PSG etch rate (Å/min.)	43	63	75
AsSG etch rate (Å/min.)	40	174	120
Etch rate selectivity			
TEOS/THOX	1.24	1.77	1.42
BSG/THOX	1.26	7.77	2.16
BPSG/THOX	1.03	8.14	1.53
PSG/THOX	1.13	2.86	1.74
AsSG/THOX	1.05	7.91	2.79

CLAIMS

1. An etching solution having a thermal oxide (THOX) film etch rate and boron phosphosilicate glass (BPSG) film etch rate at 25°C of 100Å/min or lower and a ratio of (BPSG etch rate) / (THOX etch rate) of 1.5 or lower.

2. The etching solution according to claim 1 comprising at least one member selected from the group consisting of a fluoride salt and a bifluoride salt.

3. The etching solution according to claim 1, wherein a solvent of the etching solution has a relative dielectric constant of 35 or lower.

4. The etching solution according to claim 1 comprising at least one member selected from the group consisting of an organic acid and an organic solvent having a hetero atom.

5. The etching solution according to claim 1 comprising (i) ammonium hydrogenfluoride, (ii) water and (iii) at least one member selected from the group consisting of an organic acid and an organic solvent having a hetero atom, the water being contained in a concentration of 3% by weight or lower.

6. The etching solution according to claim 1 comprising ammonium hydrogenfluoride, water and isopropyl alcohol, the water being contained in a concentration of

3% by weight or lower.

7. The etching solution according to claim 1 comprising ammonium hydrogenfluoride, water and ethanol, the water being contained in a concentration of 3% by weight or lower.

8. The etching solution according to claim 1 comprising ammonium hydrogenfluoride, water and acetone, the water being contained in a concentration of 3% by weight or lower.

9. The etching solution according to claim 1 comprising (i) ammonium fluoride and (ii) at least one member selected from the group consisting of an organic acid and an organic solvent having a hetero atom.

10. The etching solution according to claim 1 comprising (i) ammonium fluoride, (ii) water and (iii) at least one member selected from the group consisting of an organic acid and an organic solvent having a hetero atom, the water being contained in a concentration of 10% by weight or lower.

11. The etching solution according to claim 1 comprising ammonium fluoride, water and ethanol, the water being contained in a concentration of 10% by weight or lower.

12. The etching solution according to claim 1 comprising ammonium fluoride, water and isopropyl alcohol,

the water being contained in a concentration of 10% by weight or lower.

13. The etching solution according to claim 1 comprising ammonium fluoride, water and acetic acid, the water being contained in a concentration of 1.5% by weight or lower.

14. A method for producing an etched article by etching an article with the etching solution as defined in any of claims 1-13.

15. An etched article which is produced by the method of claim 14.

DECLARATION FOR USA PATENT APPLICATION

(including Design and National Stage PCT)

Attorney's Docket ID: P07222US00

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below adjacent to my name. I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled ETCHING SOLUTION, ETCHED ARTICLE AND METHOD FOR ETCHED ARTICLE, the specification of which

____ is attached hereto. (or)

__x__ was filed on November 22, 1999, [ ] and was amended on _____.

[ ] as U.S. Application No. _____ (or)

[x] as International PCT Application No. PCT/JP99/06503

I hereby state that I have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment referred to above. I acknowledge the duty to disclose information which is material to patentability as defined in Title 37, Code of Federal Regulations, § 1.56.

I hereby claim foreign priority benefits under Title 35, United States Code, § 119 (a) - (d) or §365 (b) of any foreign application(s) for patent or inventor's certificate, or §365 (a) of any PCT International application which designated at least one country other than the United States of America, listed below and have also identified below, where priority is not claimed, any foreign application for patent or inventor's certificate, or any PCT International application, having a filing date before that of the application on which priority is claimed:

Prior Foreign Application(s) (____ ADDITIONAL APPLICATIONS IDENTIFIED ON ATTACHED SHEET):

Number	Country	Day/Month/Year Filed	Priority Not Claimed
1998-332767	Japan	24/11/1998	____
_____	_____	_____	____
_____	_____	_____	____

I hereby claim the benefit under Title 35, United States Code, § 120 of any United States application(s), or §365(c) of any PCT International application designating the U.S., listed below; and insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States or PCT International application in the manner provided by the first paragraph of Title 35, United States Code, § 112, I acknowledge the duty to disclose information which is material to patentability as defined in Title 37, Code of Federal Regulations § 1.56 which became available between the filing date of the prior application and the national or PCT international filing date of this application. (___ ADDITIONAL APPLICATIONS IDENTIFIED ON ATTACHED SHEET.)

Application Serial No.	Day/Month/Year Filed	Status – patented, pending, abandoned
_____	_____	_____

I hereby appoint the practitioners of **LARSON AND TAYLOR** associated with the Customer Number provided below to prosecute this application and to transact all business in the Patent and Trademark Office connected therewith, and direct that all correspondence be addressed to that Customer Number.

CUSTOMER NUMBER: 00881

00881

PATENT TRADEMARK OFFICE

Direct all telephone calls to _____, at TEL (703) 920-7200 (Fax: 703-820-8483)

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under § 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

Full Name of Sole or First Inventor: KEZUKA Takehiko	Citizenship: Japan
Full Post Office Address: c/o Yodogawa Seisakusho, DAIKIN INDUSTRIES, LTD., 1-1, Nishihitotsuya, Settsu-shi, Osaka 566-0044, Japan	
Residence - City, State/Country (if different from P.O. address): Same as the above	JPX
SIGN AND DATE HERE: Inventor's Signature: Takehiko Kezuka	Date: May 9, 2001

Full Name of Second Joint Inventor, if any: SUYAMA Makoto	Citizenship: Japan
Full Post Office Address: c/o Yodogawa Seisakusho, DAIKIN INDUSTRIES, LTD., 1-1, Nishihitotsuya, Settsu-shi, Osaka 566-0044, Japan	
Residence - City, State/Country (if different from P.O. address): Same as the above	JPX
SIGN AND DATE HERE: Inventor's Signature: Makoto Suyama	Date: May 9, 2001

Full Name of Third Joint Inventor, if any: ITANO Mitsushi	Citizenship: Japan
Full Post Office Address: c/o Yodogawa Seisakusho, DAIKIN INDUSTRIES, LTD., 1-1, Nishihitotsuya, Settsu-shi, Osaka 566-0044, Japan	
Residence - City, State/Country (if different from P.O. address): Same as the above	JPX
SIGN AND DATE HERE: Inventor's Signature: M. Itano	Date: May 9, 2001

Full Name of Fourth Joint Inventor, if any:	Citizenship:
Full Post Office Address:	
Residence - City, State/Country (if different from P.O. address):	
SIGN AND DATE HERE: Inventor's Signature:	Date:

___ SEE ATTACHED SHEET FOR SIMILAR INFORMATION AND SIGNATURE FOR ADDITIONAL JOINT INVENTORS.